

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 788 148 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
06.08.1997 Bulletin 1997/32(51) Int. Cl.⁶: H01L 21/316

(21) Application number: 96927864.7

(86) International application number:
PCT/JP96/02335

(22) Date of filing: 21.08.1996

(87) International publication number:
WO 97/07537 (27.02.1997 Gazette 1997/10)(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: 21.08.1995 JP 212004/95

(71) Applicants:

- ASM JAPAN K.K.
Tokyo 206 (JP)
- Oki Electric Industry Company, Limited
Tokyo 105 (JP)

- YOSHIMARU, Masaki,
Oki Electric Industry Co., Ltd.
Minato-ku, Tokyo 105 (JP)

- MORI, Yukihiro,
ASM Japan K.K.
Tama-shi, Tokyo 206 (JP)

- FUKUDA, Hideaki,
ASM Japan K.K.
Tama-shi, Tokyo 206 (JP)

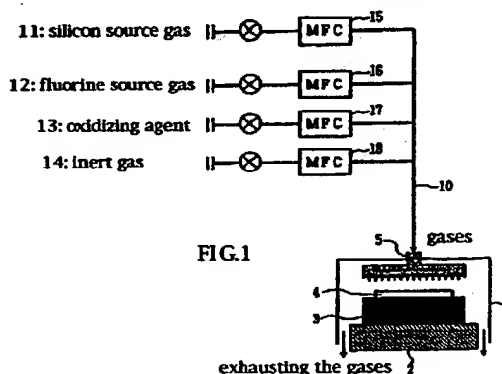
(72) Inventors:

- KOIZUMI, Satoshi,
Oki Electric Industry Co., Ltd.
Minato-ku, Tokyo 105 (JP)

(74) Representative: de Bruijn, Leendert C. et al
Nederlandsch Octrooibureau
P.O. Box 29720
2502 LS Den Haag (NL)**(54) METHOD OF PRODUCING SEMICONDUCTOR DEVICE**

(57) There is provided a method for reducing absorptivity of moisture of an insulation film made of SiOF and for achieving a highly reliable semiconductor device.

In a method for manufacturing a semiconductor device utilizing a silicon oxide film including fluorine as a layer insulation film of a semiconductor integrated circuit, an inert gas 14 is introduced in addition to source gases 11 - 13 during the formation of the silicon oxide film including fluorine.



EP 0 788 148 A1

Description

TECHNICAL FIELD

The present invention relates to a method for manufacturing semiconductor devices and, more particularly, to a method for forming a layer insulation film utilizing a silicon oxide film.

BACKGROUND ART

For example, conventional techniques in this field include that disclosed in an article "A Study on the Structure of PE-CVD SiOF Films" by Takashi Usami et al. on Shingaku Giho SDM 94-146 (November, 1994).

Silicon oxide films (SiO₂) utilizing plasma enhanced chemical vapor deposition (PE-CVD) have been commonly used as insulation films of semiconductor devices. However, a trend toward finer and more highly integrated devices has resulted in increased capacitance between lines which has an influence on the driving power of the devices.

This has resulted in an increased need for insulation films having a lower relative dielectric constant, and fluoridated (F) silicon oxide films (SiOF) have come to attention as one of such materials having a low relative dielectric constant. As disclosed in the above-mentioned article, SiOF can be formed by mixing tetraethyl orthosilicate (TEOS), oxygen (O₂), and an etching gas including fluorine (F) (e.g., C₂F₆, CF₄, NF₃, HF, etc.) in a reaction chamber under plasma discharge.

However, an insulation film made of SiOF formed using the above-described conventional method has high absorptivity of moisture and absorbs a large amount of moisture therein.

This has resulted in problems including that:

- (1) it can cause corrosion of a metal line which is a factor of a semiconductor device; and
- (2) it reduces the lifetime of a transistor which forms a factor of a semiconductor device, and this has made it difficult to manufacture semiconductor devices of high reliability.

It is an object of the present invention to eliminate the above-described problems and to provide highly reliable semiconductor devices by reducing the absorptivity of moisture of insulation films made of SiOF.

DISCLOSURE OF THE INVENTION

In order to achieve the above-described object, according to the present invention:

- (1) in a method for manufacturing a semiconductor device utilizing a silicon oxide film including fluorine as a layer insulation film of a semiconductor integrated circuit, an inert gas is introduced in addition to source gases during the formation of said silicon

oxide film including fluorine, which, as a result, makes it possible to improve the efficiency of dissociation of the material gas, thereby allowing the formation of a more uniform film;

- (2) in a method for manufacturing a semiconductor device according to the above (1), said inert gas is at least one gas selected from helium and argon, which results in an increased compressive stress of the SiOF film to allow the film to be denser; and

- (3) in a method for manufacturing a semiconductor device according to the above (1), said source gases include tetraethyl orthosilicate (TEOS), hexafluorocarbon (C₂F₆), and oxygen (O₂) used as a silicon source, a fluorine source, and an oxidizer, respectively, and the inert gas is used in an amount which is seven times or more of that of the silicon source gas, which improves the absorptivity of moisture of the film thus formed, and such an effect is further enhanced by increasing the amount of helium supplied.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a PE-CVD apparatus used for forming a SiOF layer insulation film to indicate an embodiment of the present invention.

Fig. 2 is a sectional view showing the formation of a SiOF layer insulation film to indicate an embodiment of the present invention.

Fig. 3 illustrates a compressive stress of a SiOF film relative to the amounts of helium and argon gas supplied to indicate an embodiment of the present invention.

Fig. 4 illustrates an infrared absorption spectrum of a SiOF film with 2000 Å thick measured after moistening for three hours under a condition that a temperature is 80°C and humidity is 80 % under the atmospheric pressure to indicate an embodiment of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will now be described with reference to the drawings.

Fig. 1 illustrates a PE-CVD apparatus used for forming a SiOF layer insulation film to indicate an embodiment of the present invention, and Fig. 2 is a sectional view depicting the formation of a SiOF layer insulation film to indicate an embodiment of the present invention.

With reference to Fig. 1, a reaction chamber of a parallel plated-anode type PE-CVD apparatus like the prior art is referred to generally by the numeral 10. In the reaction chamber 1, there is disposed a heater 2, a susceptor 3 on the heater 2, and a wafer 4 to be processed on the susceptor 3. A gas supply port 5 is formed in the top of the reaction chamber 1, and a gas which is a mixture of source gasses, i.e., a silicon source gas 11, a fluorine source gas 12, and an oxidizer 13 is introduced to

the gas supply port 5 through a pipe 10. Further, an inert gas 14 is supplied to cause plasma discharge which results in the formation of a film. MFCs (flow rate controllers) is designated by the numeral 15-18.

Specifically, when a silicon oxide film including fluorine is formed in the above-described PE-CVD apparatus, the introduction of the inert gas 14 in addition to the source gases 11-13 results in the formation of a fluorinated (F) silicon oxide film (SiOF) 22 on a substrate 21 which has semiconductor integrated circuits formed on the surface of a wafer 4 as shown in Fig. 2.

Thereafter, upper wiring layer 23 is formed on the SiOF film 22.

With such a configuration, by supplying an inert gas having high dissociating potential during the formation of the layer insulation film, the dissociation efficiency of each source gas can be improved to allow a uniform layer insulation film to be formed.

A second embodiment of the present invention will now be described.

Helium or argon which is a rare gas is used as the inert gas in the first embodiment. Film formation is performed with these rare gases introduced in the reaction chamber along with source gases.

In this case, the volume ratio of the source gases as a whole to helium or argon as the inert gas is desirably 3:1 or less.

Such a configuration results in an increased compressive stress of a SiOF film so as to make the film denser.

Fig. 3 illustrates a compressive stress of a SiOF film relative to the amounts of helium and argon gas supplied to indicate an embodiment of the present invention. The compressive stress (Pa: pascal) and the flow rate of each gas (sccm) are shown along the ordinate and the abscissa axis respectively.

As apparent from Fig. 3, while helium provides a higher effect, both helium and argon gas have an effect of increasing the compressive stress of the film as the supplied amount is increased, thereby making the film denser.

A third embodiment of the present invention will now be described.

As the source gases in the first embodiment, tetraethyl orthosilicate (TEOS), hexafluorocarbon (C_2F_6), and oxygen (O_2) are used as the silicon source, fluorine source, and oxidizer, respectively, under the condition as shown below and helium is used as the inert gas under the condition as shown below.

TEOS	140 cc/min.
C_2F_6	500 cc/min.
O_2	2000 cc/min.
He	1000, 2000 cc/min.

Fig. 4 shows an infrared spectrum absorption of a SiOF film with 2000 Å thick formed under the condition as described above. In Fig. 4, the broad peak around 3400 cm^{-1} represents water (H_2O) absorbed by the film.

Fig. 4 illustrates an infrared spectrum absorption of a SiOF film with 2000 Å thick measured after moistening for three hours under a condition that a temperature is 80°C and humidity is 80 % under the atmospheric pressure, to indicate an embodiment of the present invention.

The infrared spectrum absorption shown in Fig. 4 was measured after moistening for three hours under a condition that a temperature was 80°C and humidity was 80 % under the atmospheric pressure, and it indicates that the more helium is supplied during the formation of the film, the less water is absorbed by the film at the moistening test. Specifically, by supplying helium in an amount which is about seven times or more of that of TEOS as the silicon source gas during the formation of the film, the absorptivity of moisture of the film is improved.

Further, such an effect is enhanced by increasing the amount of helium supplied.

The present invention is not limited to the above-described embodiments and there may be various modifications based on the spirit of the present invention which are not intended to be excluded from the scope of the present invention.

As described above in detail, according to the present invention, the following effects can be achieved.

(1) According to the invention as set forth Claim 1, by introducing an inert gas in addition to source gases during the formation of a silicon oxide film including fluorine, the efficiency of dissociation of the material gas can be improved so as to allow the formation of a more uniform film.

(2) According to the invention as set forth Claim 2, since helium or argon gas is introduced as the inert gas, a compressive stress of a SiOF film is increased so as to allow the film to be denser.

(3) According to the invention as set forth Claim 3, since source gases include tetraethyl orthosilicate (TEOS), hexafluorocarbon (C_2F_6), and oxygen (O_2) used as a silicon source, a fluorine source, and an oxidizer, respectively, and the inert gas is used in an amount which is seven times or more of that of the source gases, the absorptivity of moisture of the film thus formed is improved.

Further, such an effect is enhanced by increasing the amount of helium supplied.

Claims

1. A method for manufacturing a silicon oxide film including fluorine to utilize as a layer insulation film of a semiconductor integrated circuit, characterized in that mixed gas including a silicon source gas, a

fluorine source gas, an oxidizer, and an inert gas is used and the amount of said inert gas is at least seven times that of said silicon source gas.

2. A method for manufacturing a silicon oxide film according to Claim 1 wherein tetraethyl orthosilicate (TEOS), hexafluorocarbon (C_2F_6), and oxygen (O_2) are used as a silicon source, a fluorine source, and an oxidizer, respectively, and Helium or Argon is used as the inert gas.

10

15

20

25

30

35

40

45

50

55

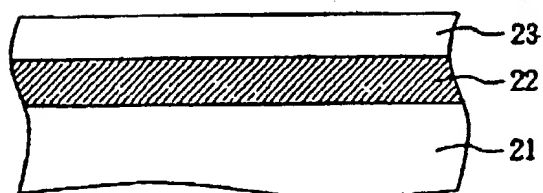
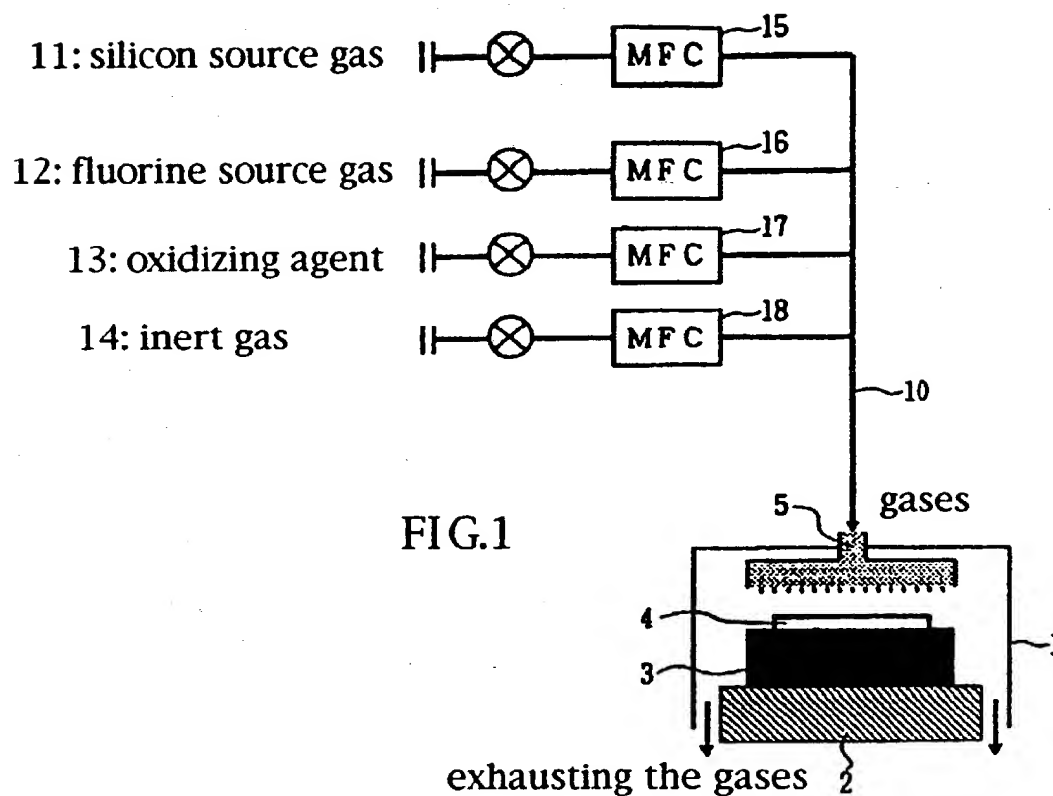


FIG.2

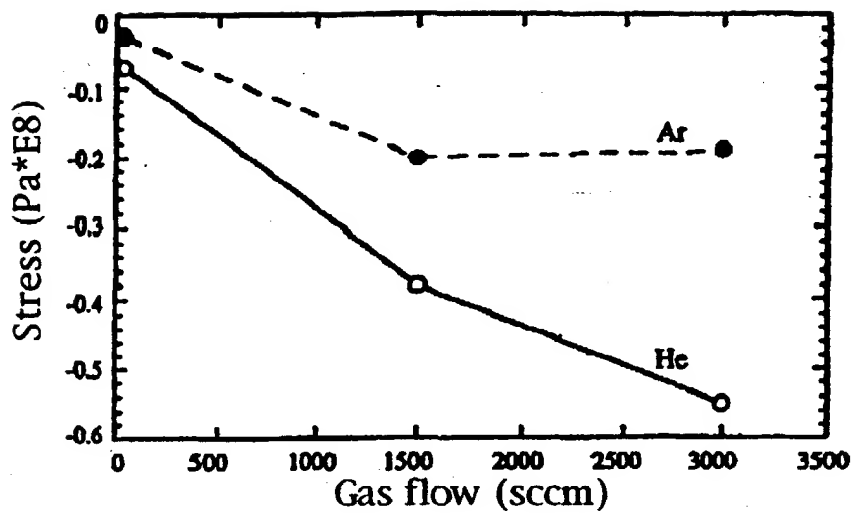


FIG.3

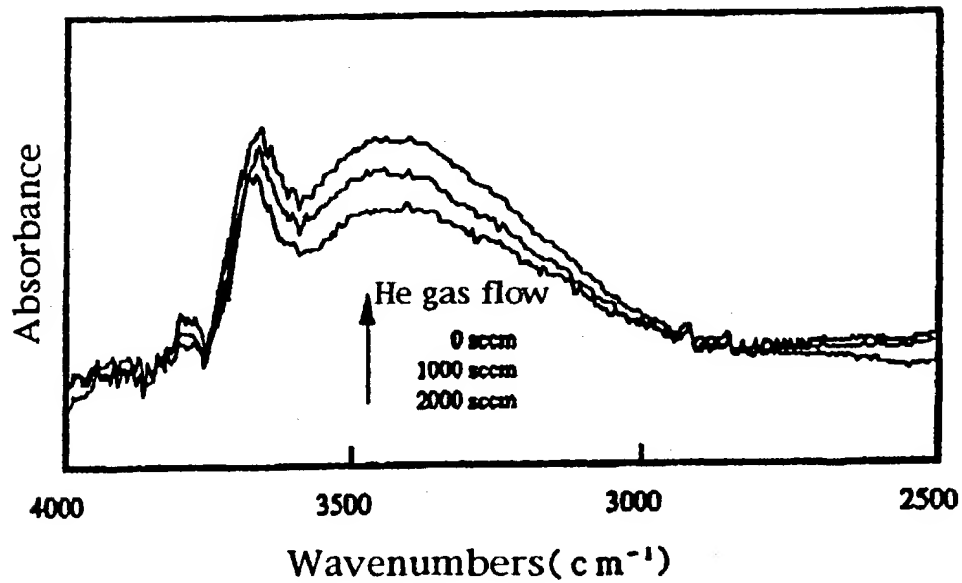


FIG.4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02335

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ H01L21/316

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ H01L21/316

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1972 - 1995

Kokai Jitsuyo Shinan Koho 1973 - 1995

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JAPANESE JOURNAL OF APPLIED PHYSICS Vol. 33 (1994) pp. 408-412, particularly, refer to "2. Experimental" and "3. Results and Discussion"	1, 2 3
X Y	Semiconductor IC technology the 45th Symposium Lecture Transactions (issued on 24. 11. 93), pp. 68-73, refer to p. 69 "2. Method" in particular	1, 2 3
A	1993 Autumn the 54th Applied Physics Society Academic Lecture Preliminary Reports, refer to p. 687 28p-X-2	1 - 3
A	JP, 7-90589, A (K.K. GTC), April 4, 1995 (04. 04. 95), Column 2, line 48 to column 3, line 3; column 4, lines 34 to 45 (Family: none)	1 - 3

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

November 6, 1996 (06. 11. 96)

Date of mailing of the international search report

November 19, 1996 (19. 11. 96)

Name and mailing address of the ISA/

Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	KIM K ET AL: "PROPERTIES OF LOW DIELECTRIC CONSTANT FLUORINATED SILICON OXIDE FILMS PREPARED BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 332, no. 1/2, 2 November 1998 (1998-11-02), pages 369-374, XP000669232 ISSN: 0040-6090	20-28	C23C16/54 C23C16/40 G02B1/10 G02B6/10 C23C16/52
Y	* paragraph '0002! *	8,29	
X	EP 0 788 148 A (OKI ELECTRIC IND CO LTD ;ASM JAPAN (JP)) 6 August 1997 (1997-08-06)	1-3,9	
Y	* column 4, line 1 - line 23; figure 4 *	4-8, 10-12	
X	TAKAMATSU A ET AL: "PLASMA-ACTIVATED DEPOSITON AND PROPERTIES OF PHOSPHOSILICATE GLASS FILM" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 131, no. 8, August 1984 (1984-08), pages 1865-1870, XP000839945 ISSN: 0013-4651	20	
Y	*Eperimental*	4-7	
Y	US 6 130 172 A (EVANS HOWARD L ET AL) 10 October 2000 (2000-10-10) * column 6, line 15 - line 22 *	10-12	
Y	US 5 660 895 A (LEE GIL S ET AL) 26 August 1997 (1997-08-26) * figure 16; example 16 *	29	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 November 2003	Examiner Ekhult, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

1

EPO FORM 1503 03.82 (P04001)



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 4 394 401 A (TAKASAKI KANETAKE ET AL) 19 July 1983 (1983-07-19) * example 2 *	1-29	
A	US 4 236 905 A (DABBY FRANKLIN W ET AL) 2 December 1980 (1980-12-02) * column 3, line 1 - line 23 *	1-29	
P,X	EP 1 134 073 A (DAINIPPON PRINTING CO LTD) 19 September 2001 (2001-09-19) * paragraphs '0033!', '0037!', '0097!', '0104!' - '0107!' *	1-4, 13, 17, 19	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 November 2003	Examiner Ekhult, H
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</div> <div>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</div>			